

PROBING EXCITED MOLECULAR COMPLEXES WITH
MULTIPHOTON AND SINGLE-PHOTON IONIZATION

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Laser and synchrotron radiation techniques have greatly expanded our ability to prepare and interrogate excited molecular complexes in order to investigate questions of molecular spectroscopy and dynamics that could not be addressed just a few years ago. Both of these active fields have expanded in many directions; however, of particular interest here is the selective preparation of well-characterized excited molecular complexes and the observation by photoelectron spectroscopy of alternative decay products as a function of the energy deposited in different rovibronic modes. This affords us the opportunity to study the interplay of electronic and nuclear modes in molecular fields at the quantum state specific level and, thus, to gain insight into fundamental mechanisms of molecular physics and chemistry.

We will discuss experiments on two molecules to illustrate these points. First, double-resonance, laser excitation of H₂ will be used to show how new information on a variety of basic molecular decay mechanisms can be obtained by selectively preparing various excited states of H₂ and monitoring the products of decay by using electron spectroscopy. Second, angle-resolved photoionization studies of CO₂ using synchrotron radiation will be used to illustrate shape-resonance-induced coupling between ionization channels and the observation of detailed dynamics of autoionization throughout the complex autoionization structure in the VUV spectrum of CO₂.

We have investigated¹ both photoionization and ion-pair formation in molecular hydrogen by using double-resonance excitation via the E,F $1\Sigma_g^+$, $v=6$ level. The energetic threshold for ion-pair formation occurs just below the H₂⁺ X $2\Sigma_g^+$, $v^+=9$ ionization threshold. The decay dynamics in this region are extremely rich, because excited levels may decay by rotational and vibrational autoionization, by predissociation to neutral H + H*($n=2,3,4$), by predissociation to the ion pair H⁺ + H⁺, and by fluorescence. In addition, the dissociative potential curve of the $2p\sigma_u3s\sigma_g$ $1\Sigma_u^+$ doubly excited electronic state crosses the H₂⁺ X $2\Sigma_g^+$

potential curve in the same energy region and is expected to significantly influence these processes. The E,F $1\Sigma_g^+$, $v=6$ level can be approximately described as the $v=2$ level of the inner well of the double minimum E,F $1\Sigma_g^+$ potential, but it has some amplitude in the outer well of the potential. Because the dominant configuration of the inner well is $1s\sigma_g2s\sigma_g$, the dominant transitions in the energy region of interest are to $(X\ 2\Sigma_g^+)np$, $v'\geq 9$ Rydberg states. The relative intensities of the $(X\ 2\Sigma_g^+)np$, $v'\geq 9$ Rydberg series converging to different rotational levels of the ion are dramatically different from those for the analogous Rydberg series with $v'\leq 2$. This observation can be explained in terms of the dependence of the transition dipole matrix elements on the internuclear distance. Autoionization of the $(X\ 2\Sigma_g^+)np$, $v'\geq 9$ Rydberg states was studied by using both conventional and constant-ionic-state photoelectron spectrometry. The results support the Δv =minimum propensity rule for vibrational autoionization. The two-color photoelectron spectrum via the E,F $1\Sigma_g^+$, $v=6$ level shows considerable intensity in the $v^+=7$ and 8 photoelectron bands both on and off resonance, in marked contrast with the single-color photoelectron spectrum obtained for the same intermediate level. This phenomenon is thought to be a manifestation of the $2p\sigma_u3s\sigma_g\ 1\Sigma_u^+$ doubly excited electronic state. The decay of the $(X\ 2\Sigma_g^+)np$, $v'\geq 9$ Rydberg states into the ion-pair continuum was studied by monitoring the H^- ion signal. Although this channel is much weaker than the ionization channel, it displays much of the same resonant structure. The electric-field dependence of the threshold for ion-pair formation was also determined.² The similarity of the long-range interaction between H^+ and H^- with that of the electron-ion system leads to analogies between the field-induced process and the processes of field ionization and forced autoionization of Rydberg states of atoms.

In the $4\sigma_g^{-1}$ photoionization channel of CO_2 , a σ_u shape resonance occurs at $h\nu \sim 40$ eV. The partial cross section and photoelectron angular distribution associated with this resonance has been studied by many groups (see Ref. 3 and references therein), and fairly good agreement between experiment and theory exists for the photoelectron asymmetry parameter, β ; however, a significant difference persists for the partial cross section for this channel. Our immediate interest is not with this channel alone, but rather with the possibility of shape-resonance-induced coupling of the σ_u shape resonance into other underlying ionization continua. Specifically, Lucchese³ has predicted that the $3\sigma_g^{-1}$ channel will be most influenced by this coupling. Indeed, we have measured the β for the $3\sigma_g^{-1}$ and have observed large deviations from single-channel calculations that are in very good agreement with the predictions of Lucchese.³ The corresponding partial cross sections, on the other hand, are not definitive.

Finally, we have recently carried out high-resolution angle-resolved photoelectron studies of the complex autoionization structure in the spectrum of CO_2 from 790 Å to 650 Å, a region which includes Rydberg series converging to the A, B, and C states of CO_2^+ . These data were taken on a 0.1 Å photon energy mesh with 0.2 Å photon bandpass and 45 meV electron energy resolution. This data set is extremely rich in information on the product vibrational states, including all three vibrational modes, as well as many harmonics and combinations. As in earlier studies (see Ref. 4 and references therein), many vibrational patterns correlate

readily with Rydberg series, while others exhibit variable vibrational patterns, presumably reflecting interactions between excitation channels. In this study, for the first time, v -dependent photoelectron angular distributions are also measured on a fine photon energy mesh throughout this spectral range. This study illustrates the wealth of dynamical information obtainable with high resolution studies using synchrotron radiation, soon to become much more routine with the development of third generation machines.

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References

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